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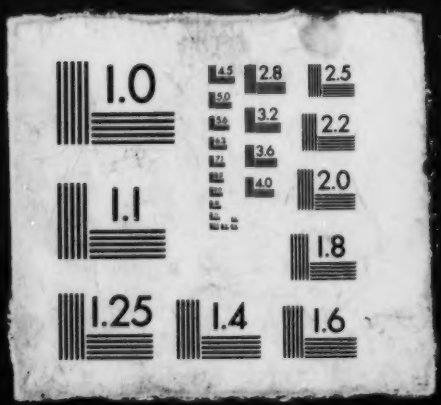

PB82-240326

Environmental Impact Assessment of Control Measures Required for Attainment of the National Ambient Air Quality Standard for Ozone

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Jun 78

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
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1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO. PB82 240326
4. TITLE AND SUBTITLE: ENVIRONMENTAL IMPACT ASSESSMENT OF CONTROL MEASURES REQUIRED FOR ATTAINMENT OF THE NATIONAL AMBIENT AIR QUALITY STANDARD FOR OZONE		5. REPORT DATE: June 1978 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS: Strategies and Air Standards Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The purpose of this assessment is to review the information presented in Air Quality Criteria for Ozone and other Photochemicals Oxidants and Control Techniques for Hydrocarbons and Volatile Organic Compounds and to present an analysis of the environmental impact of control measures required for attainment of the air quality standard for ozone.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Photochemical Oxidants Ozone Air Pollution Air Quality Standards		EPA 68A

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
	20. SECURITY CLASS *(This page)*	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

PB82-240326

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NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

Environmental Impact Assessment of Control Measures Required for Attainment of the National Ambient Air Quality Standard for Ozone

Introduction

The Clean Air Act, as amended, requires that the Administrator of the U. S. Environmental Protection Agency periodically review the basis for the ambient air quality standards. A review of the National Ambient Air Quality Standard (NAAQS) for photochemical oxidants has recently been concluded and the Air Quality Criteria for Ozone and other Photochemicals Oxidants and Control Techniques for Hydrocarbons and Volatile Organic Compounds have been reissued. The criteria document has been revised to incorporate new information about the health and welfare effects of oxidants. The control techniques documents presents available control technology based on experience and new developments since the previous publications.

The purpose of this assessment is to review the information presented in the control techniques document and to present an analysis of the environmental impact of control measures required for attainment of the air quality standard for ozone.

Background

Photochemical oxidants occur as a result of a complex series of chemical reactions in the atmosphere. Precursors of the oxidants are emitted to the atmosphere from both natural and man-made sources.

Although the natural contribution is the greater of the two, sources resultant of man's activities, in combination with favorable meteorological conditions, produce locally excessive concentrations of oxidants. A very simplified description of the atmospheric photochemistry is given by the following equations:

$$NO_2 \xrightarrow{\text{Sunlight}} NO + O \qquad (1)$$

$$O + O_2 \xrightarrow{M} O_3 + M \qquad (2)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (3)$$

$$RO_x + NO \rightarrow NO_2 + RO_y \qquad (4)$$

where M is a third body (usually N_2, O_2, or H_2O) stabilizing the molecule; R is an organic or inorganic radical; x = 1,2, or 3; and y= x - 1.[1]

Reactions 1 through 3 are very rapid and their rates are nearly equal. At steady state conditions, ozone and NO are formed and destroyed in equal quantities. The equilibrium equation is:

$$(O_3) = K \frac{(NO_2)}{(NO)} \qquad (5)$$

Thus the concentration of ozone in the polluted atmosphere is controlled by the intensity of sunlight and the ratio of NO_2 to NO. Hydrocarbons and other pollutants - such as aldehydes, ketones, chlorinated hydrocarbons and carbon monoxide - react to form peroxy radicals. These, in turn, react with nitric oxide, causing the ratio (NO_2) : (NO) to increase, and

the ozone concentration to increase.[1]

The photochemical oxidants that combine to form smog, include NO_2, O_3, and smaller concentrations of peroxyacetyl nitrates and other peroxy compounds. Efforts toward regulation of photochemical oxidants have previously attempted to deal with that entire class of pollutants. However, measurement of total oxidants is imprecise and the health and welfare effects of most of many non ozone photochemical oxidants are not known. Ozone is the most abundant member of the photochemical oxidant family occurring in the atmonphere. Ambient levels of ozone can be measured very acurately (Appendix D, 40 CFR, Part 50 for the measurement of Photochemical Oxidants) and many of the health and welfare effects of ozone are well understood. Thus, an ambient air quality standard for ozone would be more precise and meaningful than the present standard for total photochemical oxidant.

Ozone is an extremely irritating gas and cannot be tolerated by some subjects at concentrations in the range of 1960-7850 $\mu g/m^3$ (1-4ppm) for more than a few minutes. Minor throat irritation and chest congestion are caused by exposure to concentrations of approximately 590 $\mu g/m^3$ (0.3ppm) and progressively more severe respiratory effects have been measured with higher exposure concentrations. Asthmatics have been

known to experience respiratory distress at (.25 ppm) and healthy adults experience significant adverse changes in lung function at concentrations of 725 $\mu g/m^3$ (0.37 ppm). New studies have demonstrated lung function decrements in human subjects at ozone concentrations as low as 0.15 ppm and some animal studies indicate adverse effects at 0.08 ppm ozone.[2] Ozone in low concentrations are significant non-human health effects such as accelerated aging of rubber, paint, and dye, and damage to vegetation.

Environmental Impacts of Stationary Source Controls.

Strategies for control of ambient ozone are directed toward emissions of volatile organic compounds. These compounds are emitted by a variety of stationary sources and by gasoline and diesel powered vehicles. The following summary of current control technology and practice is based upon and extracted from the report "Control Techniques for Voltatile Organic Emissions from Stationary Sources",[3] which was prepared for EPA by Radian Corporation under contract No. 68-02-2608.

There are three basic methods used to control emissions of hydrocarbons and other organics from stationary sources. They are:

1. the installation of control equipment to recover or destroy the organic vapors,
2. the substitution of less photochemically reactive materials in the process, and
3. the incorporation of process and material changes that reduce or eliminate vapor emissions.

The five major technologies for the recovery or destruction of organics are: incineration, adsorption, absorption, condensation, and flaring. Each technology and the associated enviornmental impacts are summarized on the following pages.

Incineration

The control of organic emissions by combustion, is the control technology most universally applied by industry. Because of its need for supplemental fuel, incineration is most useful when the heat developed during combustion is recovered and used to meet other plant energy needs.

Afterburners, also called vapor incinerators, are devices in which dilute concentrations of organic vapors are burned with additional fuel. Afterburners oxidize organic emissions either by direct flame (thermal) incineration or by catalytic oxidation. Under the proper conditions, the firebox of a process heater or boiler may also be used as an afterburner.

Possible adverse environmental effects must be considered in choosing thermal or catalytic incineration as a means of controlling volatile organic vapor emissions. The benefits from incineration must be weighed against the adverse effects of implementing this control method.

The process stream, fuel gas, or fuel oil to be combusted in an incinerator may contain sulfur compounds. Oxidation of these compounds produces varying amounts of sulfur oxides which are then released to the

atmosphere. For an afterburner combusting a 15% LEL gas stream containing no appreciable sulfur compounds with No. 2 fuel oil, SO_2 emissions are approximately 50 ppm.

In addition, nitrogen-containing compounds may be oxidized to NO_x, increasing pollution emissions. Due to thermal fixation of air, no nitrogen compounds need be found in the fuel or waste gas to produce NO_x emissions. NO_x emissions result from all combustion processes. The estimated NO_x concentration for effluent from natural gas-fired, noncatalytic afterburners is 40 to 50 ppm.

Incineration of any halogen-containing compound causes acid formation, which is undesirable.

If a distillate fuel oil is used to fire an incinerator, particulate emissions may become an air pollution concern. An afterburner designed for the disposal of volatile organic emissions usually does not have sufficient residence time to combust organic particulates efficiently.

In catalytic incineration, the regeneration or replacement of the catalyst can present a secondary pollution problem. When the catalyst needs to be completely replaced, the used catalyst is treated as solid waste, and an acceptable means for disposal must be found. If the catalyst can be reused, the suggested cleaning or reactivation process, usually supplied by the manufacturer, requires provisions for proper disposal of any waste material.

Adsorption

Adsorption is the process by which components of a gas are retained on the surface of granular solids. The solid adsorbent particles are highly porous and have a very large surface-to-volume ratio. Gas molecules penetrate pores of the material and contact the large surface area available for adsorption. Organic vapors retained on the adsorbent are subsequently desorbed, usually with steam. Both the vapors and the adsorbent are recovered and may be reused.

Complete package adsorption systems are available from a number of manufacturers. The economic feasibility of organic vapor emission control by adsorption depends on the value of solvent recovered from the adsorbent and the cost of removing adsorbed organics from the adsorbent bed.

There are some potential environmental impacts caused by adsorption systems, including both air and water pollution. Loss of organic solvent with wastewater, oxidation product emissions with incineration, and solid waste disposal are possible results depending upon the type of adsorption system utilized.

If a steam desorption cycle is used and the recoverable organic solvents are soluble in water, then some form of water treatment or separation process is required to minimize the organic concentration in the wastewater.

Incineration can be used to control emissions from the adsorber during steam or hot air desorption. The type and amount of emission are very dependent on the nature of the exit stream.

Some process streams contain particulates which plug the void spaces in the adsorbent bed and render it ineffective much sooner than normal. This problem is solved by precleaning the gas feed stream. However, an effective means for disposing of the particulates must then be found. The disposal of spent adsorbent is also an environmental concern, but this may be necessary only once in three to five years.

Absorption

Absorption is the process in which certain constituents of a gas stream are selectively transferred to a liquid solvent. Absorption may be purely physical, in which the solute simply dissolves in the absorbent or with reagents dissolved in the absorbent.

The generally low concentrations of exhaused organics require long contact times and large quantities of absorbent for adequate emissions control. Absorption is, therefore, less desirable than adsorption or incineration, unless the absorbent is easily regenerated or the solution can be used as a process makeup stream. Absorption may be best suited for use in conjunction with other control methods such as incineration or adsorption to achieve the prescribed degree of emissions removal.

Adverse environmental effects resulting from the operation of an absorber include improper disposal of the organic-laden liquid effluent, undesired emissions from the incineration of the regenerated waste gas, loss of absorbent to the atmosphere, and increased water usage.

The liquid effluent from an absorber can frequently be used elsewhere in the process. When this is not possible, the non-regenerated absorbent effluent should be treated to provide good water quality. Such treatment may include a physical separation process (decanting or distilling) or a chemical or biological treating operation.

Regeneration consists of heating the liquid effluent stream to reduce the solubility of the absorbed organics and separate them from the absorbent. These concentrated organics can then be oxidized in an afterburner. Emissions of SO_x, NO_x, and other incomplete oxidation products may be a result, depending on the nature of the regenerated gas stream.

The control of one type of volatile organic emission can result in the emission of another at an even greater rate when liquid absorption is employed. For example, vapors of trichloroethylene can be substantially reduced in an air stream by absorption in a lean mineral oil; however, at ambient temperature the air stream leaving the absorber might contain 120 ppm mineral oil.

Use of water absorption increases plant water requirements. However, an add-on water scrubbing system will usually mean only a minimal increase in the throughput to the existing water treatment facilities in a plant.

Condensation

Condensers operate by preassurizing or lowering the temperature of an exhaust vapor thereby condensing out the organic contaminants. Condensation is usually applied in combination with other air pollution control systems. Condensers located upstream of afterburners, carbon beds, or absorbers can reduce the total load entering the more expensive

control equipment. Unless concentrated vapors are to be removed, condensation is rarely the sole means of controlling organic emission. When used alone, condensation often requires costly refrigeration to achieve the low temperatures needed for adequate control.

A condenser will create few secondary environmental problems when the condensation process is considered by itself. Problems that do arise include disposal of non-condensibles in surface condensers and refrigeration systems, and the need for proper treatment of the liquid effluent in contact condenser systems. Condensation is rarely used alone as a control method; therefore, it is imperative that all associated equipment produce effluent streams of sound environmental quality.

The non-condensible gas effluent from surface condensers is either vented to the atmosphere or further processed (e.g., via incineration), depending on the effluent composition. The coolant never contacts the vapors or condensate in the surface condenser; therefore, the recovered organic compounds are usually reusable. The condensate might not be saved if more than one compound is condensed and separation is costly. Proper treatment of the condensate is then imperative before final disposal. This also applies for the recovery of volatile organic emissions by refrigeration.

In contact condensation, the condensate is contaminated with the coolant liquid. The usual procedure is treatment of the waste stream and disposal. The amount of organic material entrained in the existing wastewater depends upon the extent of treatment.

Flares

Flares are most commonly used to incinerate waste gases from petroleum refining and petrochemical manufacturing operations. Flares are preferred when treating gas streams with sufficient heat value to attain the combustion temperature without the use of supplemental fuel. Flares are also preferred when treating gases with little recovery value, or for gases containing contaminants that make recovery unprofitable.

The operation of a flare affects the environment in the following areas: chemical and oxidation emissions, particulate emissions, thermal and visible radiation, and noise. Elevated flares are primarily intended for plant emergencies and are inherently not as efficient in the above areas as new, enclosed, ground-level flares.

Chemical emissions are the direct result in incomplete combustion of the volatile organics contained in the waste gas stream. Carbon monoxide and partially oxidized hydrocarbons such as aldehydes are known to be products of elevated flares. Because of lower design velocities, emission of unburned hydrocarbons is much lower in an enclosed, ground-level flare.

Sulfur compounds, nitrogen compounds, and other undesirable chemicals are also completely oxidized and emitted to the atmosphere. In particular, hydrogen sulfide streams are often routed to flares and burned. SO_x emissions from refinery flares average 27 lb/10^3 bbl refinery feed.

NO_x emissions from flares are also common due to direct contact of nitrogen with oxygen at the flame temperature. But NO_x emissions from

elevated flares using steam to inject air are lower than for gas-fired burners due to the lower flame temperature. A typical emission rate for a flare system in a petroleum refinery is 19 lb $NO_x/10^3$ bbl refinery feed.

Air must be well mixed with the gas at the point of combustion in a flare or soot will escape from the flare. A smokeless flame is attained when an adequate amount of air is kept well mixed at the point of combustion. This is usually accomplished by injecting steam to provide the needed turbulance.

Other emissions include thermal and visible radiation. Steam injection can reduce thermal radiation by lowering the flame temperature. Luminosity cannot be completely reduced, but enclosing a ground level flare is desirable, especially in populated areas.

Low frequency combustion noise and high frequency jet noise in flares is an environmental problem for elevated flares in populated areas. The jet noise is not a problem with ground level flares, and the combustion noise is reduced significantly.

Other control methods in many instances may completely avoid the emission of chemically reactive organic vapors. Compounds of low photochemical reactivity can sometimes be substituted for highly-reactive compounds currently in use. The resultant total organic emissions do not necessarily decrease and may increase, but the substitution of non-reactive or less reactive organic compounds can reduce urban photochemical oxidant formation. Few volatile organic compounds are of such low photochemical reactivity that they can be ignored in oxidant control programs.

The most efficient technique for controlling organic emissions is to design equipment that completely consumes the materials being processing. Improved operating and maintenance procedures can sometimes substantially reduce or eliminate organic emissions. New process technologies can reduce organic emissions by avoiding inefficient or poorly controlled operations.

Secondary environmental impacts of stationary source controls are generally insignificant if properly designed and operated, however, control systems employing internal combustion engines to drive compressors may create NO_x problems that are not justified. Such cases should be carefully evaluated to establish the net environmental benefit.

Environmental Impacts of Mobile Source Controls

Section 202 of the Clean Air Act, as amended, required substantial reduction of certain specified emission products from automobiles. The automotive industry, to achieve these reductions, chose the oxidation catalytic convertor as the primary method of emission control.

In 1974 EPA established the Catalyst Research Program to determine what, if any, new pollutants might be emitted into the atmosphere as a result of the application of this technology.[4] The effects of fuel composition and fuel additives on these emissions were also studied. Results from the EPA research program indicated that although emissions of hydrocarbons, carbon monoxide, and certain organics would be dramatically lowered, sulfuric acid aerosol emissions would increase and slight emissions of platinum, palladium, and aluminum might also be expected. EPA subsequently initiated a broad research study to examine the public health impact of catalyst-emitted sulfates, platinum, and palladium.

EPA and other researchers have continued these investigations and have included work on other emissions including manganese, ruthenium, hydrogen cyanide, ammonia, and polynuclear aromatic compounds.[5] While much of this work is still on going, results have indicated that the magnitude of these secondary impacts is not of major concern.[6] Results of studies of the emissions of various metals are nearing completion. Emissions of HCN were found to be at acceptable levels under worst-case conditions. The investigation of possible adverse health effects of ammonia emissions is now in progress. Emissions of H_2SO_4 have been found to vary widely depending upon engine and convertor mileage, engine design, mode of driving, etc. Although recent tests of California equipped autos have shown H_2SO_4 emissions as high as 136 mg/mi, recent testing of non-air-injection equipped vehicles indicates emissions of less than 10 mg/mi and air-injection equipped vehicles emit 20 mg/mi or more.[5] This recent testing also indicates that as HC and CO emissions increase with age and mileage of the equipment, H_2SO_4 emissions decline.[5] This research together with research on human health effects of H_2SO_4 is continuing and major reports of findings are expected to be available during the coming year. The ruthenium testing is precipated by the possibility that auto manufacturers are considering its use in NO_x reduction catalysts, and the fact that ruthenium oxides may be highly toxic.[5] EPA is not currently in a position to quantify what, if any, levels of ruthenium emissions would be considered significant.[5] Polynuclear aromatic compounds are primarily a concern with respect to diesel engine

emissions. However, they are also emitted by gasoline power engines. Emissions from catalyst equipped engine are substantially less than are those from noncatalyst equipped engines, thus environmental impact is favorable.[5] In summary, much research and investigative work remains to be completed prior to a clean bill of health regarding secondary impacts of oxidation catalyst; however, earlier concerns of excessive secondary impact have been lessened as the research proceeds.

A favorable secondary impact accrues from the increasing use of non-leaded gasoline in catalyst equipped automobiles. Some recently reported declines in airborne lead concentrations are probably being attributed to the increasing use of non-leaded gasoline.[7]

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